



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>6</sup> : <b>B05D 7/00, C23C 16/00, C01G 23/00, 23/047</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 96/36441</b> (43) International Publication Date: 21 November 1996 (21.11.96)</p>
<p>(21) International Application Number: PCT/US96/07886 (22) International Filing Date: 17 May 1996 (17.05.96) (30) Priority Data: 08/443,055 17 May 1995 (17.05.95) US (71) Applicant: KEMIRA PIGMENTS, INC. [US/US]; President Street Extension, Savannah, GA 31404 (US). (72) Inventors: KODAS, Toivo; 11102 San Rafael N.E., Albuquerque, NM 87122 (US). POWELL, Quint; 1144 Princeton N.E., Albuquerque, NM 87106 (US). ANDERSON, Bruce; 139 Grays Creek Drive, Savannah, GA 31410 (US). (74) Agents: HUCKETT, Gudrun, E. et al.; Robert W. Becker &amp; Associates, Suite 200, 5300 Sequoia N.W., Albuquerque, NM 87120 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. With amended claims.</p>
<p>(54) Title: COATING OF TiO<sub>2</sub> PIGMENT BY GAS-PHASE AND SURFACE REACTIONS</p> <p>(57) Abstract</p> <p>In a process for making pigment-grade TiO<sub>2</sub> coated with a metal oxide, a thermally decomposable volatile titanium-containing precursor is introduced into a reactor. The titanium-containing precursor is thermally decomposed within the reactor to form TiO<sub>2</sub> pigment particles. Subsequently, one or more thermally decomposable volatile metal-containing coating precursors are injected into the reactor. The one or more metal-containing coating precursors are reacted within the reactor to form a coating of the one or more metal oxides on the TiO<sub>2</sub> pigment particles.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

COATING OF TiO<sub>2</sub> PIGMENT BY GAS-PHASE AND SURFACE  
REACTIONS

Technical Field

5        This invention pertains to a process of  
coating titanium dioxide particles with metal  
oxides by gas-phase reaction.

Background Art

10       The gas-phase reaction of TiCl<sub>4</sub> and O<sub>2</sub> is  
used to make particulate TiO<sub>2</sub> often of a size  
useful as a white pigment. The pigment particles  
are usually not used in typical applications such  
as paint without first coating them with materials  
including, but not limited to, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and  
mixtures thereof. To coat the particles, they are  
15       typically collected from the gas and dispersed in  
a liquid where the coating is applied by  
precipitation. This liquid-phase coating process  
often results in coatings with high surfaces  
areas, high oil absorption, and non-uniform  
20       thickness.

U.S. Patent 4,803,056 describes a method  
for increasing the capacity of a titanium dioxide  
producing process. Titanium tetrachloride is  
added at a second point in the system downstream  
25       of the main inlet for titanium tetrachloride to  
increase the yield of TiO<sub>2</sub>. The process is  
exclusively used for the production of uncoated  
titanium dioxide. The addition of other reagents  
at the second point of introduction in order to  
30       produce a coating on the TiO<sub>2</sub> particles is not  
suggested or disclosed.

Hung and Katz (J. Mater. Res., 7, 1861  
(1992)) disclose a process for forming coated

- 2. -

5 particles in a flame. For example, non-pigmentary  
TiO<sub>2</sub> can be coated with SiO<sub>2</sub> in a flame reactor  
whereby TiCl<sub>4</sub> and SiCl<sub>4</sub> are added simultaneously  
into the same flame. The reaction conditions must  
be carefully adjusted such that TiO<sub>2</sub> condenses  
before SiO<sub>2</sub> in order to achieve a coating of SiO<sub>2</sub>  
on the already formed TiO<sub>2</sub> particles. It is  
difficult to reliably produce SiO<sub>2</sub>-coated TiO<sub>2</sub>  
particles of a uniform quality in terms of size  
and coating hardness with this process.

10 It is therefore an object of the present  
invention to provide a simple and reliable process  
for coating TiO<sub>2</sub> pigment particles in the gas  
phase to give coatings with low surfaces areas,  
low oil absorption, and uniform thickness.

15 Disclosure of the Invention

The process for making pigment-grade  
TiO<sub>2</sub> coated with a metal oxide according to the  
present invention is primarily characterized by  
the following steps:

20 introducing a thermally decomposable  
volatile titanium-containing precursor into a  
reactor;

thermally decomposing the titanium-  
containing precursor within the reactor to form  
TiO<sub>2</sub> pigment particles;

subsequently injecting at least one  
thermally decomposable volatile metal-containing  
coating precursor into the reactor; and

30 reacting the at least one metal-  
containing coating precursor within the reactor to  
form a coating of at least one metal oxide on the  
TiO<sub>2</sub> pigment particles.

- 3 -

Preferably, the coating is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and mixed metal oxide. The mixed metal oxide is expediently  $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$  with  $x = 0-1$  and  $y = 0-1$ .

5           The titanium-containing precursor is selected from the group consisting of  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ , and  $\text{Ti(OR)}_4$ , wherein R is an alkyl group.

10           The method advantageously further comprises the step of adding a thermally decomposable volatile aluminum-containing precursor to the titanium-containing precursor to form Al-doped  $\text{TiO}_2$ . As is well known in the art, water may also be added to control the particle size of the formed  $\text{TiO}_2$  pigment particles.

15           The metal-containing coating precursor is selected from the group consisting of  $\text{SiX}_4$ ,  $\text{AlX}_3$ , and  $\text{ZrX}_4$ , wherein X is Cl, Br or OR, R being an alkyl group. However, other metal-containing coating precursors can be used equally  
20           successfully. For example, they may be selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal  $\beta$ -diketonates,  
25           all well known to a person skilled in the art. It is also possible to use metal carbonyls, metal oxyhalides, and metal hydrides.

30           The method further comprises the step of adding a co-reactant, preferably water, to the metal-containing coating precursor. It is known to a person skilled in the art that water may be used to modify or control the reaction of the coating precursor.

- 4 -

The reactor is advantageously a tubular flow reactor.

5 The method further comprises the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor.

10 The injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of a coaxial tube of the tubular flow reactor, and a radially extending injection port.

15 In a preferred embodiment of the present invention, at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

20 The inventive method according to another embodiment further comprises the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing coating precursors downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor.

25 The coating precursors may be injected as mixtures, or separately but simultaneously at the same point in the reactor, or may be injected separately at different points in the reactor to produce mixed oxide coatings or to produce a coating comprising separate layers of metal

30 oxides. The injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the

- 5 -

tubular flow reactor, and a radially extending injection port.

5            Preferably, each separate coating layer has a thickness of 1-100 nm. Advantageously, the coating has a total thickness of 1-100 nm.

          The step of thermally decomposing includes the step of heating by fuel combustion, by conduction or by a plasma arc for initiating the formation of  $\text{TiO}_2$ .

10           The step of introducing the titanium-coating precursor includes the step of selecting a first and a second location of introduction, wherein the second location is arranged downstream of the first location.

15           The step of introducing the titanium-containing precursor and/or the step of injecting the metal-containing coating precursor may include the step of employing a carrier gas, for example, oxygen.

20           Preferably, the method further comprises the step of collecting the  $\text{TiO}_2$  pigment particles downstream of the flow reactor.

          Advantageously, the reactor is maintained at atmospheric pressure during the inventive process. It is also possible to maintain less than atmospheric pressure (vacuum) within the reactor or perform the inventive process at a pressure of 1 to 10 atm (atmospheres) within the reactor.

30           The present invention describes a gas-phase method for making coated pigment grade  $\text{TiO}_2$ . It allows multi-component coatings and multilayer coatings. The coatings produced by the inventive



- 6 -

process are dense and have low oil absorption. The inventive process eliminates the need to collect the particles before the coating can be applied thereby simplifying the manufacturing process.

5 According to the present invention  $\text{TiO}_2$  pigment particles are produced by a gas-phase reaction of titanium-containing precursors, for example,  $\text{TiX}_4$ , suspended in a gas stream and are then coated with a coating of metal oxide(s) produced by gas-phase and surface reactions of thermally decomposable volatile metal atom- or ion-containing coating reactants introduced at a single point or multiple points into a tubular flow system at a location downstream of the formation zone in which the  $\text{TiO}_2$  pigment particles are fully formed.

10 The inventive system or apparatus consists of three sections including sequentially: a tubular flow formation zone in which the  $\text{TiO}_2$  particles are formed, a zone in which the thermally decomposable volatile metal atom- or ion-containing coating reactants (precursors) are introduced into the gas stream carrying the  $\text{TiO}_2$  particles to be coated, and a coating zone in which the  $\text{TiO}_2$  particles are coated by the metal oxide(s) being formed from the metal-containing coating precursor(s).

25 In a first step, the titanium dioxide particles are formed by gas-phase reaction. Subsequently, the volatile metal-containing coating precursors are injected which react in the gas phase as well as on the surface of the



- 7 -

titanium dioxide particles to form a coating. The coated particles are then collected at the exit of the flow reactor. Thus, the invention described here relies on sequential particle formation and particle coating.

Brief Description of the Drawing

The object and advantages of the present invention will appear more clearly from the following specification in conjunction with the accompanying drawing, in which the only Figure schematically shows the system for coating particles according to the present invention for a specific embodiment.

Best Modes for Carrying out the Invention

The present invention will now be described in detail with the aid of several specific embodiments utilizing the only Figure in which a specific embodiment is illustrated.

The inventive system consists of the following components: a pigment particle generator (particle formation zone), an introduction zone for the thermally decomposable volatile metal-containing coating precursor (reactant), and a coating zone. In the particle formation zone,  $\text{TiCl}_4$  reacts with  $\text{O}_2$  to form respective  $\text{TiO}_2$  particles (illustrated as small circles). The drawing shows the introduction of three thermally decomposable volatile metal-containing coating reactants downstream of the particle formation zone:  $\text{ML}_n$ ,  $\text{M}'\text{L}_n$ , and  $\text{M}''\text{L}_n$  where M, M', M'' represent a metal atom and L represents a ligand attached to the metal atom. However, the reaction of only one coating reactant  $\text{ML}_n$  is shown. It is

- 8 -

5 schematically shown that the reaction to form the metal oxide can take place in the gas phase (formation of small particles, illustrated by small cross-hatched circles) which are then captured by the preformed  $\text{TiO}_2$  particles to form the coating or can take place at the surface of the  $\text{TiO}_2$  particles resulting in a direct coating of the  $\text{TiO}_2$  particle (the produced coating is schematically represented by cross-hatching).

10 Preferred compounds are, for example,  $\text{SiCl}_4$ ,  $\text{SiBr}_4$ ,  $\text{Si(OR)}_4$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{Al(OR)}_3$ ,  $\text{ZrCl}_4$ ,  $\text{ZrBr}_4$ , and  $\text{Zr(OR)}_4$ . It is obvious to those skilled in the art that other types of precursors of various structures can be used, for example, coating precursors with organic ligands such as metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal  $\beta$ -diketonates or coating precursors with inorganic ligands such as metal carbonyls, metal oxyhalides, and metal hydrides. The given compounds are examples only and not meant to limit the scope of the inventive process

25 The drawing shows the sequential nature of the process in which the particles are formed first, followed by introduction of the thermally decomposable volatile metal-containing coating reactants, and then coating. It is also obvious that only one or a plurality of thermally decomposable volatile metal-containing coating reactants can be used, as desired and needed for the  $\text{TiO}_2$  pigment product properties. Thus, the invention is not limited with respect to the

30

- 9 -

number of thermally decomposable volatile metal-containing coating reactants that can be used, the order in which they are introduced into the reactor, or the type of thermally decomposable volatile metal-containing coating reactant.

It is also possible to use an additional metal compound as a dopant together with the titanium-containing precursor. For example,  $\text{TiCl}_4$  as a titanium precursor can be mixed with  $\text{AlCl}_3$ , introduced into the reactor with oxygen (carrier gas) at a temperature of about 900 °C or higher, and reacted in a tubular flow system to give  $\text{TiO}_2$  particles containing Al. It is obvious to those skilled in the art that other types of dopants can be added to the titanium-containing precursor without departing from the scope of the present invention. In this context it should also be mentioned that water can be added, as is well known in the art, in order to help adjust or control the  $\text{TiO}_2$  particle size.

It is well known to persons skilled in the art that the particle formation and particle coating within the reactor occur over a short period of time. The gas stream exiting from the reactor is cooled to allow collection of the coated particles.

The gist of the present invention is the addition (injection) of a thermally decomposable volatile metal-containing coating reactant into a reactor tube at a location downstream of the zone in which the  $\text{TiO}_2$  particles are formed, but where the temperature is still high enough to cause reaction of the thermally decomposable volatile

- 10 -

metal-containing coating reactants both in the gas phase and on the surfaces of the  $\text{TiO}_2$  pigment particles.

5 It is possible to add only a single thermally decomposable volatile metal-containing coating reactant, such as  $\text{SiCl}_4$ , in order to give a coating of one material ( $\text{SiO}_2$  in the given example).

10 However, it is also possible to add two thermally decomposable volatile metal-containing coating reactants at the same time to give a single coating which is a mixed oxide of the two metals. For example,  $\text{SiX}_4$  and  $\text{AlX}_3$  can be added together resulting in a mixed oxide  $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$ ,  
15 wherein essentially any ratio between the two oxides is possible. In this case it is desirable to match the reaction temperatures of the thermally decomposable volatile metal-containing coating reactants to allow reaction at the same  
20 location in the reactor.

In another embodiment of the present invention, two or more thermally decomposable volatile metal-containing coating reactants are added sequentially to give a coating comprised of  
25 two or more layers of individual metal oxides.

The invention can be carried out in a variety of apparatus configurations. The preferred embodiment is a tubular flow system in which the thermally decomposable volatile metal-containing coating reactants are introduced from  
30 the exterior of the reactor tube into the reactor tube at points downstream of the zone in which the  $\text{TiO}_2$  particles are formed but where the

- 11 -

temperature is still high enough to cause reaction of the thermally decomposable volatile metal-containing coating reactants both in the gas phase and on the surfaces of the particles.

5                Various approaches can be used to introduce the thermally decomposable volatile metal-containing coating reactants into the reactor. For example, the thermally decomposable  
10                volatile metal-containing coating reactants can be added through a porous wall or through radially extending injection points. It is also possible to use coaxial injection. Those skilled in the art realize other methods that are also equally viable.

15                The temperature at which the thermally decomposable volatile metal-containing coating reactants are to be decomposed must be sufficiently high in order for the coating  
20                reactants to react at the surface of the  $\text{TiO}_2$  particles or for the particles of the coating material, formed in the gas phase, to be able to collide with the  $\text{TiO}_2$  pigment particles and fuse into their surfaces. Temperatures that are too  
25                low result in formation of separate particles comprised of the coating material that are not incorporated into the coating. Temperatures that are too high result in reaction of the coating  
30                material with the particle to be coated, i.e., the metal(s) of the coating material and the  $\text{TiO}_2$  particle react to form mixed metal oxide phases thus degrading the  $\text{TiO}_2$  pigment particle properties.

For the coating of  $\text{TiO}_2$  with  $\text{SiO}_2$  using

- 12 -

SiCl<sub>4</sub>, the temperature must be greater than 1300°C. When TiO<sub>2</sub> is to be coated with Al<sub>2</sub>O<sub>3</sub>, the temperature must be greater than 1100°C. For coating TiO<sub>2</sub> with a mixed Si/Al oxide, the temperature must be greater than 1200°C. However, in any case, the temperature must not be too high in order to prevent interdiffusion and/or reaction between TiO<sub>2</sub> and the coating material.

The flow reactor can be heated to the required reaction temperature by conventional methods such as fuel combustion, conduction, a plasma arc or other means well known to a person skilled in the art.

Especially for large scale production processes, it is known in the art to use the energy derived from the exothermic reaction of the Ti-containing precursor with oxygen for heating the flow reactor to the desired reaction temperature when the gaseous reactants (Ti-containing precursor and oxygen) are preheated to a suitable preheating temperature. Of course, the exothermicity of the reaction aids in reaching the required temperature in all possible process variations.

The inventive process can be carried out under various pressures. The reactor can simply be maintained at atmospheric pressure during the inventive process. It is also possible to maintain less than atmospheric pressure (vacuum) within the reactor or perform the inventive process at a pressure of 1 to 10 atm (atmospheres) within the reactor.

Example 1. Formation of TiO<sub>2</sub> particles coated with

- 13 -

SiO<sub>2</sub>.

A tubular flow reactor was used at a temperature of 1500 °C. Oxygen gas (carrier gas) was guided through TiCl<sub>4</sub> to vaporize and introduce TiCl<sub>4</sub> into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 seconds. The gas mixture reacted to form TiO<sub>2</sub> particles in the reactor.

Liquid SiCl<sub>4</sub> was vaporized by heating at 25°C and introduced as a vapor into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed the SiCl<sub>4</sub> to be introduced into the reactor in a region where the temperature was near 1500 °C. The SiCl<sub>4</sub> reacted both in the gas phase and on the surfaces of the formed TiO<sub>2</sub> particles. The gas phase reaction of the metal-containing coating precursor resulted in the formation of small metal oxide particles which were captured by the TiO<sub>2</sub> particles and incorporated into the surface as a coating by sintering. Because of the small size of the metal oxide particles, sintering was rapid. The coated TiO<sub>2</sub> pigment particles were collected on a filter after exiting the reactor.

The surface reaction resulted in the direct deposition of a uniform continuous coating with a thickness of 10 nm as shown by Transmission Electron Microscopy. The composition of the coating was confirmed by energy dispersive spectroscopy which showed only Si and O. X-ray diffraction showed only TiO<sub>2</sub> and confirmed that the coating process did not degrade the properties



- 14 -

of the pigment by forming additional undesired phases.

Example 2. Formation of  $\text{TiO}_2$  particles coated with  $\text{Al}_2\text{O}_3$ .

5           A tubular flow reactor was used at a temperature of 1500 °C. Oxygen (carrier gas) was guided through  $\text{TiCl}_4$  to vaporize and introduce  $\text{TiCl}_4$  into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 sec. The gas mixture reacted to form  $\text{TiO}_2$  particles in the reactor.

15            $\text{AlCl}_3$  was vaporized by heating at less than 250 °C and passing a carrier gas over the powder. The vapor was introduced into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed  $\text{AlCl}_3$  to be introduced into the reactor in a region where the temperature was near 1500°C.  $\text{AlCl}_3$  reacted both in the gas phase and on the surfaces of the formed  $\text{TiO}_2$  particles. The gas phase reaction of the metal-containing coating precursor  $\text{AlCl}_3$  resulted in the formation of small particles of  $\text{Al}_2\text{O}_3$  which were captured by the  $\text{TiO}_2$  particles and incorporated into the surface as a coating by sintering. Because of the small size of the  $\text{Al}_2\text{O}_3$  particles, sintering was rapid. The particles were collected on a filter after exiting the reactor.

25           The surface reaction resulted in the direct deposition of a uniform continuous coating with a thickness of 10 nm as shown by Transmission Electron Microscopy. The composition of the

- 15 -

coating was confirmed by energy dispersive spectroscopy which showed only Al and O. X-ray diffraction showed only  $\text{TiO}_2$  and confirmed that the coating process did not degrade the properties of the  $\text{TiO}_2$  pigment particles by forming additional undesired phases.

Example 3. Formation of  $\text{TiO}_2$  particles coated with  $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$ .

A tubular flow reactor was used at a temperature of 1500 °C. Oxygen (carrier gas) was guided through  $\text{TiCl}_4$  to vaporize and introduce  $\text{TiCl}_4$  into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 sec. The gas mixture reacted to form  $\text{TiO}_2$  particles in the reactor.

$\text{SiCl}_4$  was vaporized by heating at 25°C without a carrier gas, and  $\text{AlCl}_3$  was vaporized by heating at less than 250°C with carrier gas flowing over the  $\text{AlCl}_3$  powder. The streams were combined and introduced as a vapor into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed the  $\text{SiCl}_4$  and  $\text{AlCl}_3$  to be introduced into the reactor in a region where the temperature was near 1500°C.  $\text{SiCl}_4$  and  $\text{AlCl}_3$  reacted both in the gas phase and on the surfaces of the particles. The gas phase reaction resulted in the formation of small metal oxide particles which were captured by the formed  $\text{TiO}_2$  particles and incorporated into the surface as a coating by sintering. Sintering was rapid because of the small size of the metal oxide particles. The coated  $\text{TiO}_2$  pigment particles were

- 16 -

collected onto a filter after exiting the reactor.

5           The surface reaction resulted in the  
direct deposition of a uniform continuous coating  
with a thickness of 10 nm as shown by Transmission  
Electron Microscopy. The composition of the  
coating was confirmed by energy dispersive  
spectroscopy which showed only Si, Al and O. X-  
ray diffraction showed only  $\text{TiO}_2$  and confirmed  
that the coating process did not degrade the  
10       properties of the pigment by forming additional  
undesired phases.

          The present invention is, of course, in  
no way restricted to the specific disclosure of  
the specification, examples and drawings, but also  
15       encompasses any modifications within the scope of  
the appended claims.

- 17 -

CLAIMS:

1. A process for making pigment-grade  $\text{TiO}_2$  coated with a metal oxide, said method comprising the steps of:

5 introducing a thermally decomposable volatile titanium-containing precursor into a reactor;

thermally decomposing the titanium-containing precursor within the reactor to form  $\text{TiO}_2$  pigment particles;

10 subsequently injecting at least one thermally decomposable volatile metal-containing coating precursor into the reactor; and

15 reacting the at least one metal-containing coating precursor within the reactor to form a coating of at least one metal oxide on the  $\text{TiO}_2$  pigment particles.

2. A method according to claim 1, wherein said coating is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and mixed metal oxide.

3. A method according to claim 2, wherein the mixed metal oxide is  $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$ .

4. A method according to claim 1, wherein the titanium-containing precursor is selected from the group consisting of  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ , and  $\text{Ti}(\text{OR})_4$  wherein R is an alkyl group.

5. A method according to claim 1, further comprising the step of adding a thermally decomposable volatile aluminum-containing compound to the titanium-containing precursor to form Al-doped  $\text{TiO}_2$ .

6. A method according to claim 1,

- 18 -

wherein the metal-containing coating precursor is selected from the group consisting of  $\text{SiX}_4$ ,  $\text{AlX}_3$ , and  $\text{ZrX}_4$ , wherein X is Cl, Br or OR.

7. A method according to claim 6, further comprising the step of adding a co-reactant to the metal-containing coating precursor.

8. A method according to claim 7, wherein the co-reactant is water.

9. A method according to claim 1, wherein the reactor is a tubular flow reactor.

10. A method according to claim 9, further comprising the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor.

11. A method according to claim 10, wherein the injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

12. A method according to claim 10, wherein at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

13. A method according to claim 1, further comprising the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing

- 19 -

5 coating precursors downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor to produce a coating comprising separate layers of metal oxides.

14. A method according to claim 13, wherein the injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

15. A method according to claim 13, wherein each separate layer of the coating has a thickness of 1-100 nm.

16. A method according to claim 1, wherein the coating has a total thickness of 1-100 nm.

17. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating by fuel combustion for initiating the formation of  $\text{TiO}_2$ .

18. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating by conduction for initiating the formation of  $\text{TiO}_2$ .

19. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating with a plasma arc for initiating the formation of  $\text{TiO}_2$ .

20. A method according to claim 1, wherein in the step of introducing the titanium-containing precursor includes the step of selecting a first and a second location of introduction, wherein the second location is

5

- 20 -

arranged downstream of the first location.

21. A method according to claim 1, wherein the step of introducing includes the step of employing a carrier gas.

22. A method according to claim 1, wherein the step of injecting includes the step of employing a carrier gas.

23. A method according to claim 1, further comprising the step of collecting the  $\text{TiO}_2$  pigment particles downstream of the flow reactor.

24. A method according to claim 1, further comprising the step of maintaining atmospheric pressure within the reactor.

25. A method according to claim 1, further comprising the step of maintaining less than atmospheric pressure within the reactor.

26. A method according to claim 1, further comprising the step of maintaining a pressure of 1 to 10 atm within the reactor.

5 27. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal  $\beta$ -diketonates.

28. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal carbonyls, metal oxyhalides, and metal hydrides.



## AMENDED CLAIMS

[received by the International Bureau on 07 October 1996 (07.10.96);  
original claims 1, 2, 6 and 17-19 amended; remaining claims unchanged (4 pages)]

1. A process for making pigment-grade  $\text{TiO}_2$  coated with  
a metal oxide, said method comprising the steps of:

introducing a thermally decomposable volatile  
titanium-containing precursor into a reactor;

5 thermally decomposing in the presence of oxygen the  
titanium-containing precursor within the reactor to form  $\text{TiO}_2$   
pigment particles;

subsequently injecting at least one thermally  
decomposable volatile metal-containing coating precursor into the  
10 reactor; and

thermally decomposing in the presence of oxygen the  
at least one metal-containing coating precursor within the reactor  
to form a coating of at least one metal oxide on the  $\text{TiO}_2$  pigment  
particles.

2. A method according to claim 1, wherein said coating  
is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  
mixed metal oxide of at least two of the metals Si, Al, and Zr.

3. A method according to claim 2, wherein the mixed  
metal oxide is  $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$ .

4. A method according to claim 1, wherein the titanium-  
containing precursor is selected from the group consisting of  $\text{TiCl}_4$ ,  
 $\text{TiBr}_4$ , and  $\text{Ti(OR)}_4$  wherein R is an alkyl group.

5. A method according to claim 1, further comprising  
the step of adding a thermally decomposable volatile aluminum-  
containing compound to the titanium-containing precursor to form  
Al-doped  $\text{TiO}_2$ .

6. A method according to claim 1, wherein the metal-  
containing coating precursor is selected from the group consisting  
of  $\text{SiX}_4$ ,  $\text{AlX}_3$ , and  $\text{ZrX}_4$ , wherein X is Cl, Br or OR, wherein R is an  
alkyl group.

7. A method according to claim 6, further comprising the step of adding a co-reactant to the metal-containing coating precursor.

8. A method according to claim 7, wherein the co-reactant is water.

9. A method according to claim 1, wherein the reactor is a tubular flow reactor.

10. A method according to claim 9, further comprising the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor.

11. A method according to claim 10, wherein the injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

12. A method according to claim 10, wherein at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

13. A method according to claim 1, further comprising the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing coating precursors downstream of a  $\text{TiO}_2$ -formation zone of the tubular flow reactor to produce a coating comprising separate layers of metal oxides.

14. A method according to claim 13, wherein the injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

15. A method according to claim 13, wherein each separate layer of the coating has a thickness of 1-100 nm.

16. A method according to claim 1, wherein the coating

has a total thickness of 1-100 nm.

17. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating by fuel combustion for initiating the formation of  $\text{TiO}_2$ .

18. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating by conduction for initiating the formation of  $\text{TiO}_2$ .

19. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating with a plasma arc for initiating the formation of  $\text{TiO}_2$ .

20. A method according to claim 1, wherein in the step of introducing the titanium-containing precursor includes the step of selecting a first and a second location of introduction, wherein the second location is arranged downstream of the first location.

21. A method according to claim 1, wherein the step of introducing includes the step of employing a carrier gas.

22. A method according to claim 1, wherein the step of injecting includes the step of employing a carrier gas.

23. A method according to claim 1, further comprising the step of collecting the  $\text{TiO}_2$  pigment particles downstream of the flow reactor.

24. A method according to claim 1, further comprising the step of maintaining atmospheric pressure within the reactor.

25. A method according to claim 1, further comprising the step of maintaining less than atmospheric pressure within the reactor.

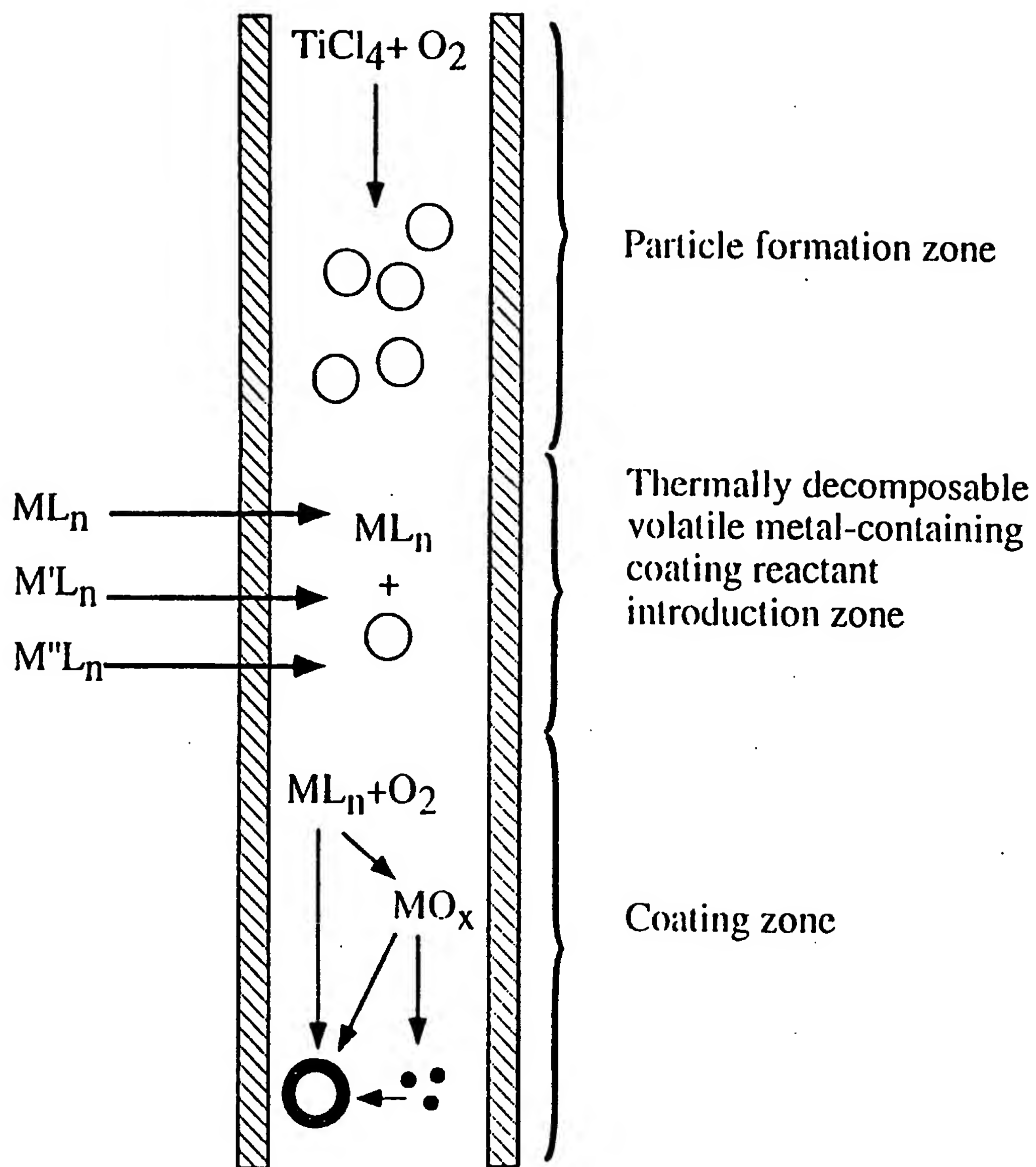
26. A method according to claim 1, further comprising the step of maintaining a pressure of 1 to 10 atm within the reactor.

5

27. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal  $\beta$ -diketonates.

28. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal carbonyls, metal oxyhalides, and metal hydrides.

1 / 1



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/07886

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 7/00; C23C 16/00; C01G 23/00, 23/047

US CL :427/212, 215, 248.1; 423/598, 610, 611, 612, 613, 614

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/212, 215, 248.1; 423/598, 610, 611, 612, 613, 614

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS. Search terms: pigment, titanium, oxide, dioxide, metal, coating, vapor, deposition

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,512,219 (STERN ET AL.) 19 May 1970, col 2, line 45 to col 4, line 56.	1-28
Y	US, A, 4,050,951 (PICCOLO ET AL.) 27 September 1977, col 2, lines 39-56; col 3, lines 12-17.	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

• Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	Z	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

22 JULY 1996

Date of mailing of the international search report

14 AUG 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SHRIVE BECK

Telephone No. (703) 308-0661